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7 An Automated Method for Preparing and Calibrating
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9 Electrochemical Concentration Cell (ECC) Ozonesondes
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32

33   Abstract

34

35   In contrast to the legacy manual method used to prepare, condition, and calibrate the Electrochemical

36   Concentration Cell (ECC) ozonesonde an automated digital calibration bench similar to one developed

37   by MeteoSwiss at Payerne, Switzerland was established at NASA's Wallops Flight Facility and

38   provides reference measurements of the same ozone partial pressure as measured by the ECC. The

39   purpose of an automated system is to condition and calibrate ECC cells before launching on a balloon.

40   Operation of the digital calibration bench is simple and real-time graphs and summaries are available to

41   the operator; all information is archived. The parameters of interest include ozone partial pressure,

42   airflow, temperature, background current, response, and time (real and elapsed). ECC cells, prepared

43   with 1.0 percent solution of potassium iodide (KI) and full buffer, show increasing partial pressure

44   values when compared to the reference as partial pressures increase. Differences of approximately 5-6

45   percent are noted at 20.0 mPa. Additional tests with different concentrations revealed the Science Pump

46   Corp (SPC) 6A ECC with 0.5 percent KI solution and one-half buffer agreed closer to the reference

47   than the 1.0 percent cells. The information gained from the automated system allows a compilation of

48   ECC cell characteristics, as well as calibrations. The digital calibration bench is recommended for ECC

49   studies as it conserves resources.

50

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1. Introduction

Measurement disagreement between similar or identical instruments seems to be an historical problem. Intercomparisons are generally conducted when new instruments are introduced and when operational changes or improved procedures become available. Such comparisons should be made under the same environmental conditions and include a reference instrument as an aid for checking the accuracy and reliability of the instruments. This would be ideal as a standard procedure. Unfortunately, balloon-borne ozone reference instruments are not usually available, mostly because they are too expensive for other than occasional use or to expend on non-recoverable balloon packages. Ozonesonde pre-flight calibrations are conducted, however these are basically single point calibrations made prior to its release. An automated system designed to condition and calibrate the Electrochemical Concentration Cell (ECC) ozonesonde was fabricated at Wallops Flight Facility. The automated system can condition the ECC prior to flight and, if desired, provide calibration over a wide range of ozone partial pressures. This system, designated the digital calibration bench, enables consistent conditioning and calibration of the ECC along with measurements of a reference value. In this paper the term ECC refers only to the Science Pump Corp. (SPC) 6A ECC ozonesonde, although the automated system can accommodate the Environmental Science (EnSci) ozonesonde as well.

There are a variety of ground-, aircraft-, satellite-, rocket-, and balloon-borne instruments available to measure the vertical structure of atmospheric ozone and its total content. These instruments operate on different principles of measurement (Fishman et al, 2003; Kohmyr, 1969; Krueger, 1973; Holland et al, 1985; Hilsenrath et al, 1986; Sen et al, 1996). Although their spatial distribution is limited, balloon-borne Electrochemical Concentration Cell (ECC) ozonesondes have had a key role as a source of truth for the other instruments and for establishing algorithms necessary for the retrieval of satellite observations. Manual preparation of the ECC requires hands-on contact by an operator.

Reducing subjectivity is important and was considered serious enough to engage in the fabrication of the automated system. The user is prompted throughout the calibration process while utilizing real-time graphs and summaries. The digital calibration bench provides consistent preparation procedures. ECC measured ozone partial pressures vs. reference partial pressures are discussed and the results corroborated with dual ECC comparisons at Wallops Island. During implementation of the digital calibration bench, beta testing provided the dual ECC measurements used in this paper for demonstration purposes. Operational use at Wallops Island was intermittent and only provided a limited number of ECC preparation records between 2009 and 2017, when bench components began to fail.

87 Notwithstanding efforts to enhance ECC performance (Smit et al, 2004, 2007, 2014; Kerr et al, 1994;

88 Johnson et al, 2002; Torres, 1981) there remain uncertainties. The accuracy of the ECC is estimated at

89 5-10 percent and also varies with altitude (Deshler etr al, 2017; Smit and ASOPOS Panel, 2014).

90 However, standardization of ozonesonde preparation methods has improved and better data quality

91 control (Smit et al, 2014) and the homogenization of the ozone data (Deshler et al, 2017; Smit et al,

92 2013) have raised the level of ozonesonde usefulness. Uncertainties also arise from poor compensation

93 for the loss of pump efficiency; erroneous background current; variable motor speed; solution loss from

94 turbulent cathode cell bubbling; air flow temperature error and whether measured at the proper location;

95 and, the use of the appropriate potassium iodide (KI) concentration. Understanding the influence these

96 parameters have on the ozonesonde measurement capability is particularly important. The digital

97 calibration bench is able to measure these parameters in a consistent way over a range of partial

98 pressures.

99

100 2 Digital Calibration Bench Description and Operational Procedure

101

102 2.1 Description

103

104 The computer-controlled preparation and calibration bench fabricated at NASA Wallops Flight Facility

105 borrows from the design of a bench developed by MeteoSwiss scientists B. A. Hoegger and G. Levrat

106 at Payerne, Switzerland. The MeteoSwiss digital calibration bench was first available in 1995 and

107 continues to be used and is updated periodically. The MeteoSwiss and Wallops digital calibration

108 benches are functionally similar but are not identical in design. A comparable bench furnished by

109 MeteoSwiss to the meteorological station at Nairobi, Kenya has been in use since 2018. The Wallops

110 Island ozone site was interested in the digital bench because of its capability to provide precise and

111 repeatable preparation of ECC's, and its automated feature requires less interaction with the ECC then

112 the manual preparation method. The Wallops Island digital bench was undergoing development

113 between 2005-2008 and used operationally only to prepare ECC's between 2009-2017.

114

115 Throughout the history of ECC ozonesonde performance, the concentration of the KI solution has been

116 questioned (Thornton and Niazy, 1982; Barnes et al, 1985; Johnson et al, 2002; Sterling et al, 2018). In

117 the late 1960's and early 1970's the recommendation to use 2.0 percent solution was unchallenged. In

118 the mid-1970's the concentration was changed to 1.5 percent, and in 1995 the KI solution was changed

119 once more to 1.0 percent. Employing the Wallops digital calibration bench enables adjustment of the

120 datasets obtained with the different concentrations to be homogenized to improve the consistency of the

121 measurements of the long-term database. The digital calibration bench allows consistent, computer-

122 controlled preparation of ECC instruments. The calibration bench accurately measures the ozone

123 reaching the ECC cells while a Thermo Environmenmtal, Inc. (TEI) ozone generator provides the

124 source of ozone at partial pressures between 0.0 and 30.0 mPa. A second TEI instrument accurately

125 measures the ozone sent to the ECC, providing a reference value. Thus, performance comparisons are

126 possible without expending costly instruments.

127

128 The Wallops digital calibration bench, shown in Fig. 1, consists of three major components: 1) mass

129 flow meter to control air flow, 2) an ozone generator and analyzer (UV photometer), and 3) computer

130 necessary to automate the timing of the programmed functions and process the data. Another important

131 component, the glass manifold, enables the simultaneous distribution of the air flow to the ECC's and

132 the UV photometer. The manifold also is a buffer maintaining constant air flow and inhibiting flow

133 fluctuation. A graphical user interface controls the various input and output functions using an interface

134 board and communications portal enabling synchronous communication protocols. A signal

135 conditioning box allows connections to the ECC's analog signals that are conditioned with custom

136 electronic components. Minor but necessary components include pressure and temperature sensors, and

137 valves and solenoids to direct the flow of laboratory grade air. Calibration validity is accomplished by

138 comparing the measured ECC ozone partial pressure against a reference partial pressure obtained with

139 the UV photometer (TEI Analyzeer).

140

141 Fig. 2, from an unpublished technical note (Baldwin, private communication), illustrate the steps

142 necessary to achieve a consistent calibration. By following the sequential flow diagram shown in Fig. 2,

143 upper panel, the operator can better understand the sequence of tests. Each shape in the diagram is

144 associated with a graphical window displayed on the monitor, as are notices that pop-up to instruct or

145 direct the operator. The computer controlled digital bench follows the ECC preparation procedure in

146 place at NASA Wallops Island at the time of the system's fabrication. Each ECC is recognized by its

147 manufacturing date and serial number and includes the manufacturers test data. Changes to the steps are

148 possible anytime through software reprogramming. The preparation sequence begins by verifying

149 whether ECC cells are new or were previously conditioned. A different path is followed for either

150 condition. New cells are flushed with high ozone prior to manually adding KI solution. Cells previously

151 having had solution added skip over the high ozone step to determine the first background current.

152 Following the first background check the remaining steps are completed. Other measurements

153 accumulated with the digital bench include motor voltage, motor current, pump temperature, and linear

154 calibration at seven levels (0.0-30.0 mPa). Program steps are displayed on the computer monitor with

155 real-time information. All data are archived and backup files maintained.

156

157   Fig. 2, lower panel, illustrates the functional diagram detailing the essential operation of the digital

158   calibration bench. Software control is shown in blue and air flow in green. Laboratory zero-grade dry

159   air or desiccated compressed air is introduced into the TEI ozone generator where a controlled amount

160   of ozone is produced. The ozone flows simultaneously to the ECC cells and to the TEI Model 49C

161   ozone analyzer. The analyzer contains the UV photometer that provides the reference partial pressure.

162

163   The digital bench reads the air flow from a Hasting mass-flow meter permitting a precise flow rate to be

164   determined. The mass-flow is then converted to volume-flow by the conventional conversion formula.

165   The volume flow rate measurement was found to be comparable to the flow rate determined with the

166   volumetric bubble flow meter. The digital calibration bench uses the Hasting Mass-Flow Meter model

167   ENALU with a HS500m transducer with a maximum mass-flow-range of 500 [scc/min].. In contrast,

168   the manual method uses a stop watch to estimate when 100 mL of air has flowed into a chamber. An

169   experienced operator, using a volumetric bubble flow meter is able to measure the time to less than 1

170   second. Tarasick et al (2016) points out that the operator uncertainty when reading the bubble flow

171   meter is about 0.1-0.3 percent. Further, the manual method requires that the effect of moisture from the

172   bubble flow meter's soap solution be accounted for; flow rates determined with the digital calibration

173   bench do not require a correction for moisture. Unfortunately, the calibration bench cannot determine

174   the pump efficiency correction (PEC); this is taken into account differently. For a number of years, the

175   ECC's PEC was physically measured at Wallops Island using a specially adapted pressure chamber

176   (Torres, 1981). This system is no longer available. However, from its many years of use an extensive

177   number of measurements are available. A sample of 200 pressure chamber measurements were

178   averaged to obtain a unique PEC that was adopted for use at Wallops Island.

179

180   After eliminating deficiencies and improving functionality the automated system was tested while

181   obtaining research data, primarily comparisons between different KI solution concentrations.

182   Calibration from 0.0 mPa to 30.0 mPa generally exceeds the nominal range of atmospheric ozone

183   partial pressure. Calibration steps are made in 5.0 mPa increments but larger or smaller increments are

184   possible with minimal software reprogramming. Differences between ECC and reference

185   measurements, if seriously large, provide an alarm to possibly reject the ECC, or after further study the

186   differences between the ECC and reference calibration might be considered as a possible adjustment

187   factor that would be applied to observational data.

188

189   2.2 Operational Procedure

190

191   ECC preparation procedures at Wallops Island are carried out five to seven days prior to preparing the

192   ECC for flight. The pump, anode and cathode cells, and Teflon tubing are flushed with high amounts of

193   ozone to passivate their surfaces and is followed by flushing with zero-grade dry air followed by filling

194   of the cells. The cells are stored until ready to be used.

195

196   Operation of the automated system is simple, requiring only a few actions by the operator that include

197   obtaining the first background current, air flow, 5 µA or high ozone (170 nb) test, response test, second

198   background current, linear calibration between 0.0 mPa and 30.0 mPa, and the final background

199   current. As indicdated in Fig. 2, upper panel, two cells can be conditioned nearly simultaneously. i.e.,

200   the program alternates measurements between ECC's.

201

202   The operator must first determine whether the cell being conditioned had already been filled with KI or

203   never was filled. Whatever the status of the cell (wet or dry) the operator enters the identification

204   information before proceeding. When a new, or a dry cell is to be processed the digital calibration bench

205   initiates high ozone flushing. The program alerts the operator to turn on the high ozone lamp after which V3 of

206   Fig. 2, lower panel, is switched to high ozone. The unit checks that ozone is flowing and after 30 minutes the

207   program switches to zero air for 10 minutes and V3 switches back to the ozone generator. When completed, the

208   operator is prompted by an instructional message on the monitor screen to fill the anode and cathode cells with

209   the proper concentrations of potassium iodide (KI) solution, i.e., the cathode cell is filled first with 3 mL of 1.0

210   percent KI solution followed, after a 10 minute delay, by filling the anode cell with a saturated KI solution. The

211   cells are stored until ready for further conditioning and calibration before being used to make an observation.

212   Considering that the ECC cell had been filled earlier with solution the digital bench instruction by-

213   passes the high ozone flushing. Ozonesonde identification is entered, as above. The operator, after fresh

214   KI has been added to the cell, is prompted on the monitor screen to begin the first background current

215   measurement. In either case, whether a dry cell for which flushing is complete, or a wet cell ready for

216   calibration, the procedure starts with clicking the OK button displayed on the monitor screen. After 10

217   minutes of dry air the background current is recorded. The background current record contains the

218   following information: date, time in 1-2 second intervals, motor current, supplied voltage, pump

219   temperature, and cell current. As the measurement is being made identical information is displayed

220   graphically on the monitor. Following the background test all further steps are automatic.

221

222   Continuing to follow the steps outlined in Fig. 2, upper panel, the measurement of the air flow is accomplished

223   on one ECC pump at a time by switching V1, shown in Fig. 2, lower panel, to the mass flow meter and at the

224   same time V2 is switched to the glass manifold (ozone generator). When completed, V1 is switched back to the

225   glass manifold and V2 is switched to the flow meter and the flow rate of the second cell is carried out. The air

226   flow is output in sec/100 ml. The information stored includes: date, time in seconds at intervals of 7-8 seconds,

227   mass flow meter temperature, atmospheric pressure, flow rate, and supply voltage.

228

229   Measuring the response of the ECC to ozone decay requires setting the ozone generator to produce 17.0 mPa

230   ozone partial pressure (approximately 5 uA). As ozone is produced the ozone level increases until the set level is

231   reached. The elapsed time to reach this level is noted. The 17.0 mPa of ozone is the reference level used to

232   initiate the response test. After recording 17.0 mPa of ozone for 10 minutes the ECC response check begins. To

233   measure the response, the cells would have to be switched to zero air quicker than the cell responds. This is

234   accomplished by switching both cells (assuming two cells are being calibrated) to the mass flow meter, the

235   source of zero air. This is more efficient than setting the generator to zero and waiting for the manifold and

236   residual ozone in the system to reach the zero level. Thus, V1 and V2 of Fig. 2, lower panel, are switched to the

237   mass flow meter for immediate zero air and the program triggers a timer. The decreasing ozone is measured and

238   recorded at five points used to reflect the cell response. As the ozone decays, measurements at 3-4 second

239   intervals provide a detailed record of the response while also being displayed real-time on the monitor. From the

240   detailed record the program selects five points (1, 2, 3, 5 and 10 minutes) successively that are used to calculate

241   the response of ozone change that should be 80-90 percent lower than the reference of 17.0 mPa. V1 and V2 are

242   switched back to the ozone generator and the next 10-min background current measurement begins. The response

243   record contains the following: date, time in seconds, motor current, supply voltage, temperature, mass flow, cell

244   current, and atmospheric pressure. Data are displayed on the monitor in real-time.

245

246   The ECC cells have been conditioned and are ready for the linear calibration. The 0.0 mPa to 30.0 mPa

247   calibration is performed. Step changes begin with 0.0 mPa, followed by measurements at 5.0, 10.0, 15.0, 20.0,

248   25.0, and 30.0 mPa. Each step requires approximately 2-3 minutes to complete allowing time for the cell to

249   respond to each ozone step change. The linear calibration includes the reference measurement made

250   simultaneously with the ECC measurement. After the upward calibration reaches the 30.0-mPa level the

251   calibration continues downward, to 0.0 mPa. The measurements are displayed on the monitor for the operators

252   use and also sent to an Excel file. Generally, the downward calibration experiences small differences from the

253   upward calibration. The available test data reveals that the downward calibrations are always higher than the

254   upward calibrations. Between 5.0 mPa and 25.0 mPa the downward calibrations of the 1.0 percent KI solution

255   are 0.8 mPa to 1.0 mPa higher than the upward calibration. The 0.5 percent solution downward calibration varies

256   between 0.5 mPa and 0.9 mPa for the same partial pressures. Only the upward calibrations are used. Following

257   the linear calibration, the final background current is obtained. This requires 10 minutes of zero grade dry air

258   before making the measurement. The data are recorded in a summary file that contains the supply voltage, motor

259   current, flow rate, pump temperature, response, and the background currents.

260

261   3 Digital Calibration Bench Practical Application

262

263   Repetitive comparison operations can be carried out with the digital calibration bench as often as

264   necessary. This could result in a potential cost saving as there would be no need to expend radiosondes,

265   ECC's, and balloons. The testing with the digital calibration bench is limited to the ranges of pressures

266   and temperatures at sea level and would be an imprecise representation in the upper altitudes.

267

268   3.1 Digital Calibration Bench (General)

269

270   Quasi-simultaneous testing of two ECC's is possible, enabling comparisons of different concentrations

271   of KI solutions. Comparison of 2.0-, 1.5-, 1.0-, and 0.5- percent KI concentrations were carried out on

272   the digital bench demonstrating that agreement with the ozone reference value improved with lower

273   concentrations. In an earlier paper Johnson et al (2002), using SPC and EnSci ECC's demonstrated

274   similar changes occurred when testing various solution concentrations that also included varying

275   amounts of buffer. Only the SPC 6A ECC's with 1.0 percent KI solution and full buffer (1.0%,1.0B)

276   and 0.5 percent KI solution and one-half buffer (0.5%,0.5B) concentrations are discussed here.

277

278   During the checkout of the digital calibration bench ECCsondes were calibrated in pairs and included

279   different KI solutions. Tests indicated the pressure and vacuum measurements were nominal, some

280   insignificant variation occurred but was not a cause for concern. Pump temperatures, controlled by the

281   room air temperature, varied 0.1ºC to 0.2ºC. Motor currents showed some variation, some measured

282   over 100 mA, suggesting a tight fit between the piston and cylinder. For example, one ECC motor

283   current initially was 100 mA, a second measurement a week later the reading was 110 mA, a final

284   reading after running the motor for a short time was 96.5 mA. Flow rates fell within the range of 27 to

285   31 seconds per 100 ml, a range comparable to flow rates manually measured with a bubble flow meter.

286   Background currents were consistent. The lowest background current allowed by the digital bench is

287   0.0044 µA. The final background currents obtained with the digital bench often were somewhat higher

288   than background currents experienced with manual preparation, generally about 0.04 µA. Although 0.4

289   µA is relatively small it is possible the higher background current value results from the ECC's

290   residual memory following exposure to the high ozone concentration during the previous linear

291   calibration step. The final background currents, obtained manually immediately prior to an ECC

292   balloon release, were in the range between 0.01 and 0.02 µA. Finally, the response of all the cells was

293   good, falling within the required 80 percent decrease within less than one minute. Graphically checking

294   a small sample of high-resolution responses found some variation as the ozone decayed.

295

296   3.2 Calibration and Potassium Iodide (KI) Solution Comparisons

297

298   As a practical example of the usefulness of the digital calibration bench is its capability to nearly

299   simultaneously obtain measurements from two ECC's, one prepared with (1.0%,1.0B) and the second

300   with (0.5%,0.5B). The recommended KI solution strength to be used with the SPC 6A ECC's is 1.0

301   percent the with full buffer (Smit and ASOPOS PANEL, 2014). Conditioning of the ECC's followed

302   the steps given in Fig. 2, upper and lower panels. In the free stratosphere ozone partial pressures usually

303   range from 15.0 mPa to 20.0 mPa. Linear calibrations to 30.0 mPa are obtained, although a lower range

304   may be reprogramed.

305

306   Figure 3 is a graphical example of differences between the reference ozone measurement and the

307   measurements of (1.0%,1.0B) and (0.5%,0.5B) KI concentrations. A sample of 18 digital bench

308   measurements were averaged to provide a representative set of differences. The close proximity

309   between the curves shown in the figure render the standard deviation lines too small, also they overlay

310   each other to some extent. The standard deviations have been added to the figure for greater clarity. The

311   variations, although small, indicate greater variability with the (1.0%,1.0B) KI solution. Fig. 3 suggests

312   that the two concentrations measured nearly identical amounts of ozone between 0.0 mPa and 8.0 mPa.

313   Both curves begin to separate and diverge above 8.0 mPa. The averaged data at 10.0 mPa indicate that

314   (1.0%,1.0B) is 0.36 mPa, or 3.6 percent higher than the reference and (0.5%,0.5B) is 0.04 mPa, or 0.4

315   percent higher; at 15.0 mPa the difference is 0.67 mPa, or 4.3 percent and 0.17 mPa or 1.1 percent

316   higher, respectively; at 20.0 mPa the difference for (1.0%,1.0B) is 1.11 mPa, or 5.5 percent and

317   (0.5%,0.5B) is 0.48 nb or 2.4 percent higher. A check at the 30.0 mPa level indicated (1.0%,1.0B) was

318   6.8 percent above the reference and (0.5%,0.5B) was 3.2 percent above. The ECC with (0.5%,0.5B) KI

319   concentration is closer to the reference than (1.0%,1.0B) KI . Both ECCs' partial pressure curves have a

320   slope greater than 1 trending toward higher amounts of ozone when compared to the reference value as

321   ozone partial pressure increases. It is clear that the (1.0%,1.0B) KI solution increases at a faster rate

322   than the (0.5%.0.5B) solution. Johnson et al (2002) have explained the effect of different KI solution

323   concentrations as well as the side effects from the buffers used. Their study of the standard (1.0%,1.0B)

324   solution indicated the ECC can report higher ozone amounts, up to 5-7 percent under constant ozone

325   conditions and can also increase the ozone amount to higher values from the buffer reactions. Fig. 3

326   indicates that the 1.0 percent KI measurement is further from the reference than the 0.5 percent KI. The

327   percentage difference between the two KI concentrations is virtually constant at 3.2 percent, or in terms

328   of a ratio between the two solutions, 0.968. Referring to the SPC ozonesondes compared during

329   BESOS, Deshler et al (2017, Fig.5 and Table 2) indicate non-linearity between the (0.5%,0.5B) and

330   (1.0%,1.0B) KI solutions and similar ratio values, 0.970/0.960 .

331

332   The digital calibration bench turned out to be an ideal tool to obtain repeated ECC calibrations. The

333   digital bench can calibrate two ECC's nearly simultaneously reducing the need to expend costly dual-

334   ECC balloons. A negative aspect, possibly, is that calibration at sea level cannot provide knowledge of

ECC behavior under upper altitude conditions. Eleven ECC pairs were calibrated over a period of three weeks. Two ECC's were prepared with (1.0%,1.0B) and (0.5%,0.5B) KI solutions. A number of time-separated calibrations were conducted with the expectation the resulting calibrations would be repeatable week-to-week. The cells were flushed and fresh KI solutions were used with each weekly test. Calibration over the full range, 0.0-30.0 mPa was carried out, Changes that might be due to improper preparation and conditioning procedures were not considered since, by definition, the digital bench is consistent in how ECC's are prepared. Consideration also must be given to the fact that the ECC sensor has a memory that may have an effect of inhibiting repeatability. The individual weekly calibrations showed varying results. Some calibrations showed an increase each week while other calibrations did not. An average of the data showed small increases week-to-week but these were too small to be significant. In essence no particular pattern was evident suggesting that calibrations on a week-to-week schedule would not be repeatable

To bring the ECC measurements into correspondence with the reference suggests that downward adjustment should be applied to each curve. When a large sample of similar digital bench measurements are obtained it should be possible to design a table of adjustments relative to ozone partial pressure that could be used to adjust ozonesonde measurements. However, since the calibrations are made at sea level such an adjustment table would not be able to account for the influence of upper atmospheric pressure and temperature. Nevertheless, any adjustment, seemingly, would be in the right direction and would aid in obtaining more representative ozone values.

Although digital bench calibration comparisons are instructive, important comparisons have been made between ECC's and reference instruments using other methods. ECC measurement comparability have been quantified through in situ dual instrument comparisons (Kerr et al, 1995; Stubi et al, 2008; Witte et al, 2019), laboratory tests at the World Ozone Calibration facility at Jülich, Germany (Smit et al, 2004, 2007, 2014) and by occasional large balloon tests such as BOIC (Hilsenrath et al, 1986), STOIC (Kohmyr et al, 1995) and BESOS (Deshler et al, 2008). BESOS provided important performance information about the SPC 6A ECC and the EnSci ozonesondes. However, these complicated large balloon experiments that seem to occur every 10 years are expensive. The environmental chamber used in the Jülich tests (Smit et al, 2007) covers a full pressure range but is also expensive to use. The purpose here is to show a calibration method that is simple to use and provides calibrations that include useful reference values, and is complementary to other methods, such as employed in the Jülich Ozone Sonde Intercomparison Experiment (Smit et al, 2004; Smit et al, 2007).

369   In the 1998-2004 period the Wallops ozone station released a number of dual-ECC balloons, twelve

370   pair successfully provided measurements to 30 km, and higher. The ECC's were attached about 35

371   meters below the balloon and each ECC separated a distance of 2 meters. Each pair was composed of

372   an ECC with (1.0%,1.0B) and (0.5%,0.5B) KI solutions. The profiles were averaged, and are displayed

373   in Fig. 4. It can be noted in the figure that the mean (0.5%,0.5B) solution reveals less ozone being

374   measured than that of the (1.0%,1.0B) solution. Near the 65-70 hPa level the (0.5%,0.5B) ECC begins

375   to report increasingly less ozone with increasing partial pressure than the (1.0%,1.0B) ECC. A similar

376   feature was noted in Fig. 3 where the separation of the ECC's with different concentrations occur with

377   increasing partial pressure. Fig. 4 shows the maximum ozone partial pressure level was about 14.0 mPa,

378   near 22 hPa, where the (0.5%,0.5B) KI solution measured approximately 1.0 mPa, or 7 percent less

379   ozone than the ECC with the (1.0%,1.0B) KI concentration. This difference is approximately 4 percent

380   higher than the result given by the digital calibration bench results of Fig.3, where, at 15.0 mPa, the

381   difference between the (1.0%,1.0B) KI and (0.5%,0.5B) KI is 3.2 percent. Dobson measurements of

382   total ozone compared with total ozone derived from each of the ECC profiles used to the obtain the

383   average profiles shown in Fig. 4 were, on average, in excellent agreement with (0.5%,0.5B). The total

384   ozone difference between the Dobson (309.5 DU) and (1.0%,1.0B) (330.4 DU) is 20./9 DU; between

385   the Dobson and (0.5%,0.5B) (308.3 DU) was 1.2 DU.

386

387   Given that the digital bench tests revealed the (0.5%,0.5B) KI solution is in close agreement with the

388   reference measurement than the (1.0%,1.0B) solution suggested that a KI solution with a weaker

389   concentration may, possibly, give closer agreement. A small number of dual ECC tests were carried out

390   with a solution of 0.3 percent with one-third buffer (03%,0.3B). Six sets of ECC's were prepared for

391   calibration. Each dual ECC test consisted of one ECC prepared with (1.0%,1.0B) KI solution and one

392   with (0.3%,0.3B) KI solution. The digital bench comparison result disclosed the (1.0%,1.0B) result

393   replicated the earlier results discussed above. As assumed, the lower concentration was nearly equal to,

394   or slightly less than the reference. Average values and standard deviations derived from the six tests are

395   shown in Fig. 5. Although the 0.3 percent solution might appear to be a better choice additional tests

396   are necessary.

397

398   4 Summary

399

400   The concept of an automated method with which to pre-flight condition and calibrate ECC ozonesondes

401   was originally considered by MeteoSwiss scientists over 20 years ago. Drawing on their expertise, a

402   facility designated as the digital calibration bench was fabricated at NASA Wallops Flight Facility

403   between 2005-2008. The digital bench was put to use immediately to study ECC performance, conduct

404   comparisons of different KI concentrations, enabled ECC repeatability evaluation, as well as calibrating

405   the ECC over a range of partial pressures, including associated reference values. Tests conducted with

406   the digital bench were performed under identical environmental conditions. The digital bench

407   eliminates the expense and time associated with making similar tests in the atmosphere.

408

409   Early use of the digital bench was to calibrate ECC's, prepared with (1.0%,1.0B) KI solution, over a

410   range of partial pressures from 0.0 mPa to 30.0 mPa. Comparison between ECC's with (0.5%,0.5B) and

411   (1.0%,1.0B) KI solution and simultaneously obtained reference values revealed the two KI solution

412   strengths were measuring more ozone than the reference. There was an increasing difference between

413   the ECC's and the reference as the partial pressure increased. For example, the ECC measurements

414   slope upward to increasingly larger differences from the reference ozone measurements, i.e., increasing

415   from 4.3 percent higher partial pressure at 15.0 mPa (Fig. 3) to about 7 percent higher at 30.0 mPa.

416

417   Results from the digital bench also corroborate differences found between SPC 6A ECC'c flown on

418   dual-instrument flights at Wallops Island. The difference between ozonesondes at a pressure of 22 hPa

419   showed the (0.5%,0.5B) ECC to be about 1.0 mPa lower than the (1.0%,1.0B) ECC.

420

421   The digital calibration bench provides a capability to apply a variety of test functions whereby the

422   valuable information gathered helps to better understand the ECC instrument. Evaluating SPC ECC

423   performance using an automated method diminishes the requirement for expensive comparison flights.

424   The tests performed, i.e., KI solution differences, calibrations over a time period, and dual-instrumented

425   balloon flights, were consistent, giving similar results. The tests described in this paper are simply

426   examples of the utility of the digital bench. Furthermore, the digital calibration bench preparation

427   facility potentially could contribute to an understanding of separating ECC measurement variability

428   from atmospheric variability. Thus, the automated conditioning and calibration system provides

429   valuable information, and as a useful tool should continue to be a valuable aid.

430

431   5 Data Availability

432   Data are available from the authors.

433

434   6 Author Contribution

435   The first author acquired and prepared the data for processing and the second author was instrumental

436   in certifying the digital calibration bench was working properly. Both contributed equally to manuscript

437   preparation.

438

7 Competing Interests

The authors declare they have no conflict of interest.

8 Disclaimer

None

9 Acknowledgments

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10 References

Barnes, R. A., Bandy, A. R., and Torres, A. L.: Electrochemical Concentration Cell ozonesonde accuracy and precision, J. Geophys. Res., Vol. 90, No. D5, 7881-7887, 1985.

Deshler, T., Mercer, J. L., Smit, H. G. J., Stubi, R., Levrat, G., Johnson, B. J., Oltmans, S. J., Kivi, R., Thompson, A. M., Witte, J., Davies, J., Schmidlin, F. J., Brothers, G., and Sasaki, T.: Atmospheric comparison of electrochemical cell ozonesondes from different manufacturers, and with different cathode solution strengths: The Balloon Experiment on Standards for Ozonesondes, J. Geophys. Res., 113, D04307, https://doi.org/10.1029/2007JD008975, 2008.

Deshler, T., Stubi, Rene, Schmidlin, Francis J., Mercer, Jennifer L., Smit, Herman G. J., Johnson, Bryan J., Kivi, Rigel, and Nardi, Bruno,: Methods to homogenize electrochemical concentration cell (ECC) ozonesonde measurements across changes in sensing solution concentration or ozonesonde manufacturer, Atmos. Meas. Tech., 10, 2021-2043, https://doi.org/10.5194/amt-10-2021-2017, 2017.

Fishman, J., Wozniak, A. E., and Creilson J. K.: Global distribution of tropospheric ozone from satellite measurements using the empirically corrected tropospheric ozone residual technique: Identification of the regional aspects of air pollution, Atmos. Chem. And Phys. Discussions, 3, pp 1453-1476, 2003.

Hilsenrath, E. W., Attmannspacher, W., Bass, A., Evens, W., Hagemeyer, R., Barnes, R. A., Komhyr, W., Maursberger, K., Mentall, J., Proffitt, M., Robbins, D., Taylor, S., Torres, A., and Weinstock, E.: Results from the Balloon Ozone Intercomparison Campaign (BOIC), J. Geophys. Res., Vol 91, 13,137-13,152, 1986.

Holland, A. C., Barnes, R. A., and Lee, H. S.: Improved rocket ozonesonde (ROCOZ-A) 1: Demonstration of Precision, Applied Optics, Vol. 24, Issue 19, 3286-3295, 1985.

Johnson, B. J., Oltmans, S. J., and Vömel, H.: Electrochemical Concentration Cell (ECC) ozonesonde pump efficiency measurements and tests on the sensitivity to ozone of buffered and unbuffered ECC sensor cathode solution,. J. Geophys. Res., Vol 107, No D19, 4393, doi: 10.1029/2001JD000557, 2002.

Kerr, J. B. et al: The 1991 WMO international ozonesonde intercomparisons at Vanscoy, Canada. Atmospheres and Oceans, 1994.

Komhyr, W. D.: Electrochemical concentration cells for gas analysis, Ann. Geophys., Vol 25, No 1, 203-210, 1969.

Komhyr, W. D., Barnes, R. A., Brothers, G. B., Lathrop, L. A., and Opperman, D. P.: Electrochemical Concentration Cell ozonesonde performance evaluation during STOIC,1989, J. Geophys. Res., 100, D5, 9231-9244, 1995.

Krueger, A. J.: The mean ozone distribution from several series of rocket soundings to 52 km at latitudes 58°S to 64°N., PAGEOPH 106,1, 1272-1280, 1973.

Proffitt, M. H., and McLaughlin, R. J.: Fast-response dual-beam UV absorption ozone photometer suitable for use on stratospheric balloons, Rev. Sci. Instru., 54, 1719-1728, 1983.

Sen, B., Sheldon, W. R., and Benbrook, J. R.: Ultraviolet-absorption photometer for measurement of ozone on a rocket-boosted payload, Applied Optics, Vol 35, No. 30, 6010-6014, 1996.

Smit, H. G. J., and Sträter, W.,: JOSIE2000, Jülich Ozone Sonde Intercomparison Experiment: The 2000 WMO international intercomparison of operating procedures for ECC ozone sondes at the

environmental simulator facility at Jülich, WMO Global Atmospheric Watch, Report No. 158 (WMO TD No. 1225). 2004.

Smit, H. G. J., Straeter, W., Johnson, B., Oltmans, S., Davies, J., Tarasick, D. W., Hoegger, B., Stubi, R., Schmidlin, F. J., Northam, E. T., Thompson, A., Witte, J., Boyd, I., Posny, F.: Assessment of the performance of ECC-ozonesondes under quasi-flight conditions in the environmental simulation chamber: Insights from the Juelich Ozone Sonde Intercomparison Experiment (JOSIE), J. Geophys Res., 112, D19306, doi:10.1029/2006JD007308, 2007.

Smit, H.G.J., and ASOPOS panel (2014), Quality assurance and quality control for ozonesonde measurements in GAW, WMO Global Atmosphere Watch report series, No. 121, 100 pp., World Meteorological Organization, GAW Report No. 201 (2014), 100 pp., Geneva. [Available online at https://library.wmo.int/pmb_ged/gaw_201_en.pdf]

Sterling, C. W., B. J. Johnson, S. J. Oltmans, H. G. J. Smit, A. F. Jordan, P. D. Cullis, E. G. Hall, A. M. Thompson, and J. C. Witte (2018), Homogenizing and estimating the uncertainty in NOAA's long -term vertical ozone profile records measured with the electrochemical concentration cell ozonesonde, Atmos. Meas. Tech, 11, 3661-3687, https://doi.org/10.5194/amt-11-3661-2018.

Tarasick, D.W., J. Davies, H.G.J. Smit and S.J. Oltmans (2016), A re-evaluated Canadian ozonesonde record: measurements of the vertical distribution of ozone over Canada from 1966 to 2013, Atmos. Meas. Tech. 9, 195-214, doi:10.5194/amt-9- 195-2016.

Torres, A. L., ECC ozonesonde performance at high altitudes: pump efficiency, NASA Technical Memorandum 73290, 10 pp, 1981.

Witte, Jacquelyn C., Thompson, Anne M., Schmidlin, F. J., Northam, E. Thomas, Wolff, Katherine R., and Brothers, George B., The NASA Wallops Flight Facility digital ozonesonde record: reprocessing, uncertainties, and dual launches. Doi.org/10,1029/2018JD0030098, 2018.

11 Figures

Fig01. Illustration of the digital calibration bench showing operational configuration and mounting

543   position of two ECC ozonesondes. The major components include ozone generator and analyzer,

544   computer, flow meter, and glass manifold.

545

546   Fig02. Digital calibration bench diagrams: a) sequential steps, and b) functional steps.

547

548   Fig03. Simultaneous comparison of ECC ozonesondes prepared with (1.0%,1.0B) [blue] and

549   (0.5%,0.5B) [red] KI solution concentrations. The reference curve is shown in black. Calibrations are

550   made in 5.0 mPa steps from 0.0 mPa to 30.0 mPa.

551

552   Fig04. Average ozone profiles from 12 pairs of SPC 6A ECC ozonesondes indicating at the 22 hPa

553   pressure level that the (0.5%,0.5B) ECCs' measured 0.7-0.8 mPa less ozone, approximately 5 percent

554   less, than the (1.0%,1.0B) ECCs'.

555

556   Fig05. Digital calibration bench results between (1.0%,1.0B) solution, blue curve, and (0.3%,0.5B)

557   solution, red curve; the reference curve is shown in black.

558   Fig 01.

559

DIGITAL CALIBRATION BENCH

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Manual insertion of KI solution required

566   **The system consists of a computer, mass flow meter, TEI 49C ozone generator, TEI 49C ozone analyzer, and incidental equipment.**

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571   **The TEI generator and analyzer are calibrated each month using a primary standard 3-meter long-path photometer.**

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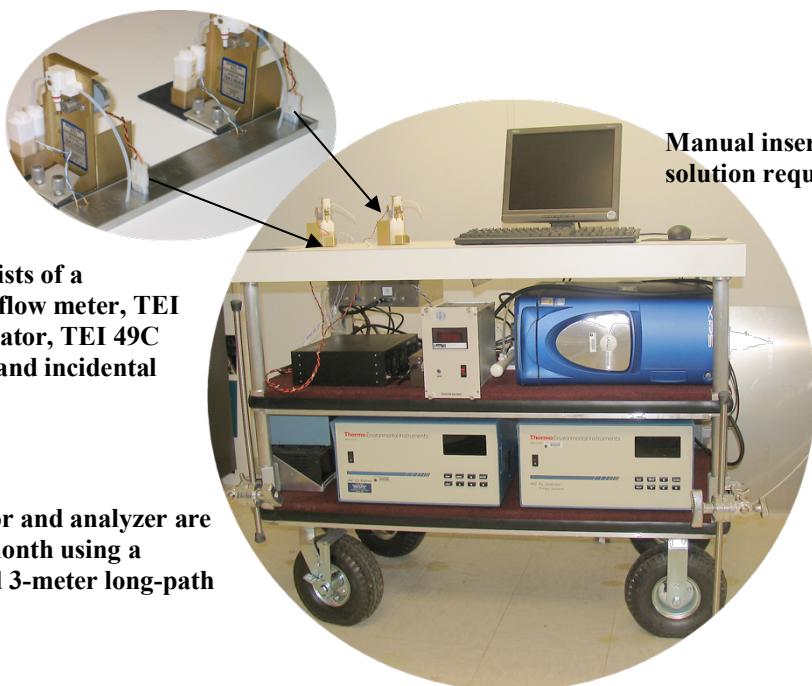
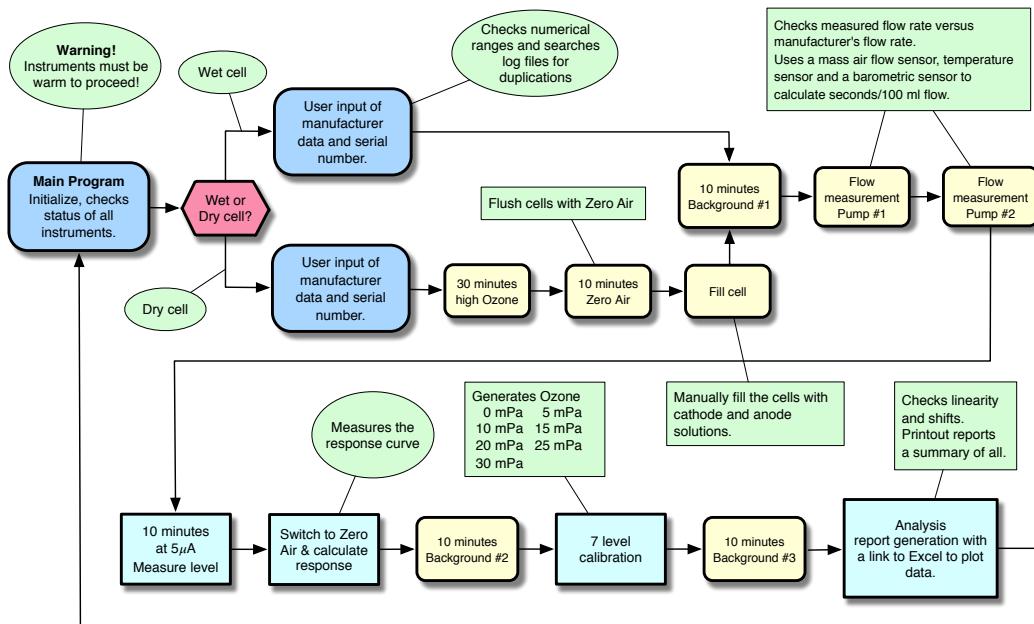

576   Fig 02.

ECC Calibration System Sequential Flow Diagram

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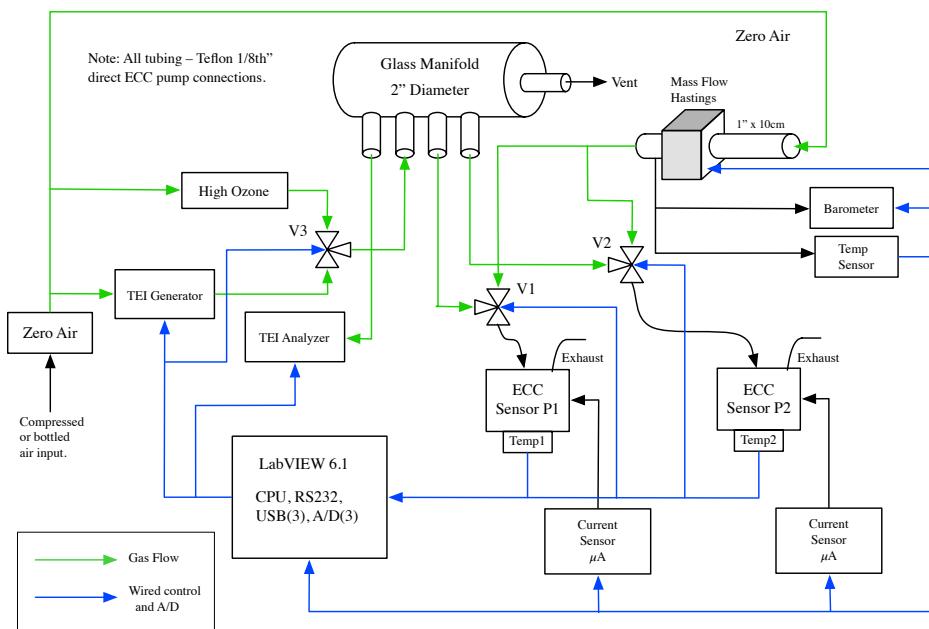
Functional Diagram Ozonesonde Calibration Test Bench

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584   Fig 03.

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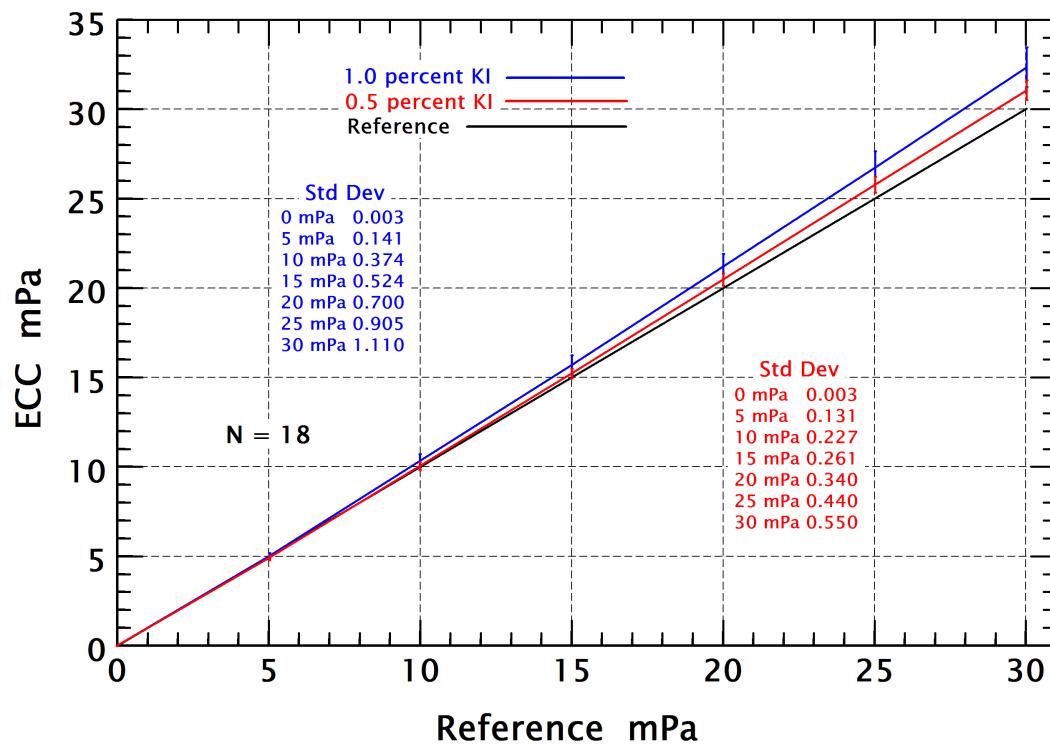
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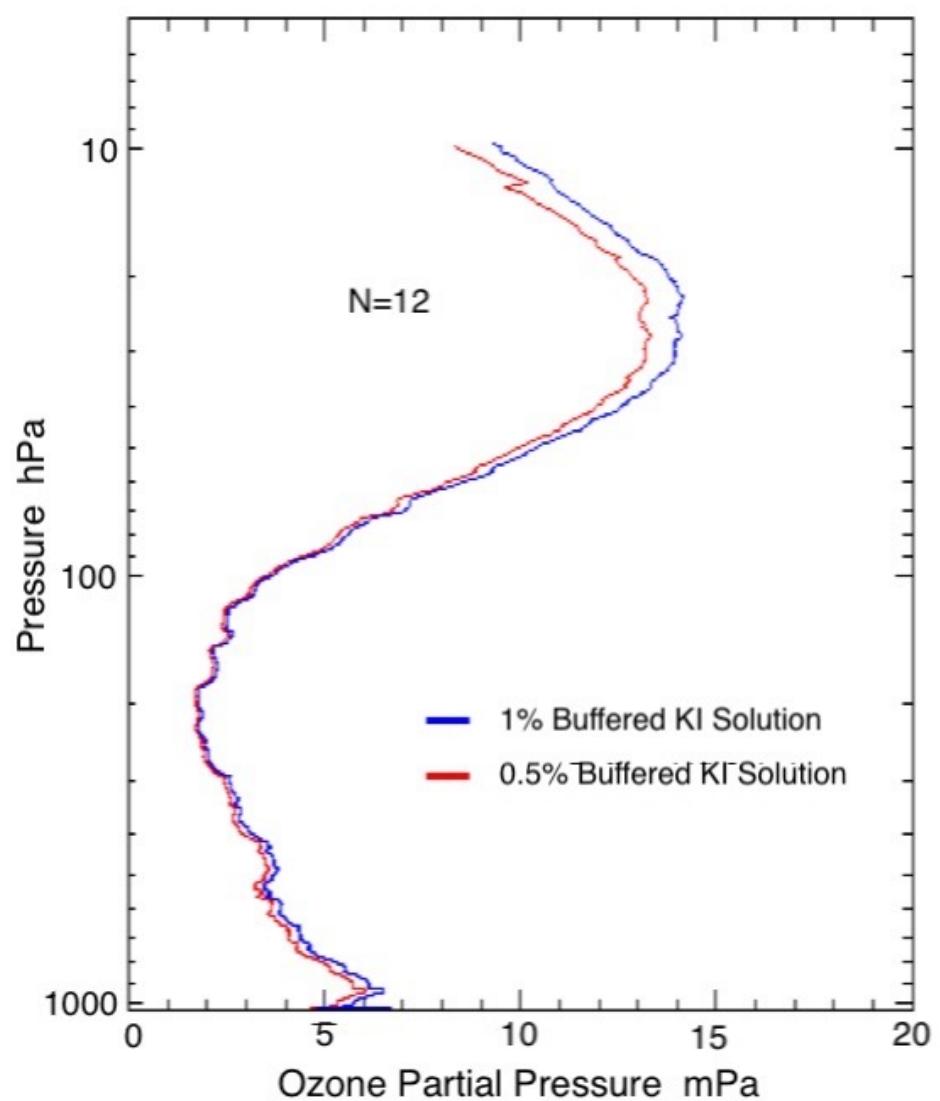
587   Fig 04.

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590   Fig 05.

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